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Sequential competitive sorption and desorption of chlorophenols in organoclay

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Abstract−Single- and bi-solute sorption and desorption of 2-chlorophenol (2-CP) and 2,4,5-trichlorophenol (2,4,5-TCP) in montmorillonite modified with hexadecyltrimethyl-ammonium (HDTMA) were investigated by sequential sorption and desorption. Effect of pH on the sequential sorption and desorption was investigated. As expected by the magnitude of octanol : water partition coefficient (K_{ow}), both sorption and desorption affinity of 2,4,5-TCP was higher than that of 2-CP at pH 4.85 and 9.15. For both chlorophenols, the protonated speciation (at pH 4.85) exhibited a higher affinity in both sorption and desorption than the predominant deprotonated speciation (about 80% and 99% of 2-chlorophenolate and 2,4,5-trichlophenolate anions at pH 9.15, respectively). Desorption of chlorinated phenols was strongly dependent on the current pH regardless of their speciation in the previous sorption stage. Freundlich model was used to analyze the single-solute sorption and desorption data. No appreciable desorption-resistant (or non-desorbing) fraction was observed in organoclays after several sequential desorptions. This indicates that sorption of phenols in organoclay mainly occurs via partitioning into the core of the pseudo-organic medium, thereby causing desorption nearly reversible. In bisolute competitive systems, sorption (or desorption) affinity of both chlorophenols was reduced compared to that in its single-solute system due to the competition between the solutes. The ideal adsorbed solution theory (IAST) coupled with the single-solute Freundlich model was positively correlated with the bisolute sequential competitive sorption and desorption equilibria.

Key words: Chlorophenols, Competition, Desorption, Ideal Adsorbed Solution Theory, Organoclay, Sorption

INTRODUCTION

Natural clays such as bentonite and montmorillonite are inherently hydrophilic due to the hydration of inorganic cations existing in the interlayers of clay. As a result, these clays are not effective sorbents to remove the hydrophobic organic compounds (HOCs) in an aqueous system. Organoclays can be prepared by exchanging inorganic cations on the clay surface by organic cations with long hydrocarbon chains such as hexadecyltrimethylammonium (HDTMA) cation [Xu and Boyd, 1995]. The intercalated organic cations may expand the interlayer of clay and form a pseudo-organic phase that increases the sorption capacity of HOCs from water. Organoclays can provide a wide range of applications in wastewater treatment and permeable reactive barriers [Boyd et al., 1988]. Contaminant immobilization using organoclay coupled with *in situ* biodegradation would provide a comprehensive restoration technology to permanently eliminate target organic contaminants [Burris and Antworth, 1992; Nye et al., 1994; Crocker et al., 1995; Witthuhn et al., 2005].

A few studies have investigated the sorption and desorption behavior of ionizable organic compounds (IOCs) in organoclays under controlled pH. IOCs can exist as either neutral or deprotonated species depending on solution pH. Boyd et al. [1988] reported the sorption of pentachlorophenol (PCP) onto the HDTMA-smectite at pH 5.5 and 10. The two isotherms were found to be nearly identical, even though the PCP (pK_a=4.75) dissociates to pentachlorophenolate anions at pH 10. We believe that the maximum equilibrium concentration (about 4 mg/L) they employed in obtaining the two isotherms was too low to discern pH-dependent sorption isotherms. Stapleton et al. [1994] studied the sorption of PCP between pH 4 and 8.5 onto HDTMA-montmorillonite. Sorption isotherms covering rather wide concentration ranges were found to be linear at low pH and nonlinear at high pH, with the sorption affinity decreasing by three times as pH changed from 4 to 8.5. Dentel et al. [1995] investigated the influence of pH on the single-solute sorption of phenol and trichlorophenol onto montmorillonite modified with dimethyldistearylammonium cation followed by partial re-exchange with Ca^{2+}. Sorption affinity of both solutes was found to increase as the neutral protonated species became predominant by lowering pH. Kim et al. [2001] reported the single-, bi- and trisolute sorption of 2-chlorophenol, 3-cyanophenol, and 4-nitrophenol onto the HDTMA-montmorillonite at pH 7.0 and 11.5 over wide concentration ranges. An increase in sorption affinity was observed as solution pH decreased. Sorption affinity of each solute in multisolute systems was reduced compared to that in a single-solute system due to the competition between solutes. Studies conducted so far have been limited to *sorption* equilibrium using the conventional, *nonsequential*-type batch methodology. Only a few studies have reported on the effect of pH on the sequential sorption and desorption of chlorophenols in organoclay [Kim et al., 2002].

Our group has extensively investigated the sorption and desorption kinetics [Kim et al., 2005] and the single- and multisolute competitive sorption of phenolic compounds onto organoclay [Kim et al., 1996, 2003; Lee et al., 1997; Kwon et al., 1998; Huh et al., 1999; 2000; Shin and Song, 2005; Song and Shin, 2005]. The Langmuir competitive model (LCM) and IAST coupled to single-solute sorption model were used to predict bisolute competitive sorption [Kim et al., 1999; Yang et al., 2003]. However, IAST coupled to the single-

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solute sorption and desorption model was not attempted to predict *sequential*-type sorption and desorption equilibria.

In this study, the sorption and desorption of chlorinated phenols (2-CP and 2,4,5-TCP) in HDTMA-montmorillonite clay were investigated. 2-CP and 2,4,5-TCP were chosen as model sorbents because they are similar in molecular structure but widely different in solubility and hydrophobicity (i.e., K_{ow} value). The purpose of this study was to determine the effect of pH on the sorption and desorption equilibria under controlled pHs (4.85 and 9.15). Sorption and desorption behaviors were investigated over a wide range of solute concentrations by performing sequential sorption and desorption. Bi-solute competitive sorption and desorption equilibria were predicted by employing the ideal adsorbed solution theory (IAST). The existence of desorption-resistant fraction in HDTMA-montmorillonite was also investigated by using sequential-type batch sorption and desorption methodology.

MATERIALS AND METHODS

1. Materials

Aqueous solutions of 2-CP (Aldrich Chemical Co., 99+%) and 2,4,5-TCP (Aldrich Chemical Co., 98+%) were prepared in an electrolyte solution containing 1 mM $CaCl_2 \cdot 2H_2O$, 0.5 mM $MgCl_2$, and 200 ppm NaN_3. The solution pH was controlled at 4.85 and 9.15 using acetate (0.02 M CH_3COOH and 0.03 M CH_3COONa) and Borax (0.01 M $Na_2B_4O_7 \cdot 10H_2O$) buffer solutions, respectively. All reagents were of analytical grade and were used without further purification. The physicochemical properties of the chlorinated phenols used in this study are listed in Table 1.

The impurities of the montmorillonite-KSF (Aldrich Chemical Co.) were removed by a digestion method using H_2O_2 [Van Olphen, 1977] and by washing it several times with distilled water at 60 °C. The clay suspension was filtered with 0.22 μm membrane filter, and the filtrate was examined for its impurities with a UV-spectrophotometer (Hewlett Packard, 8452A). The washed montmorillonite was settled, dried in an oven at 60 °C for 24 hours, and stored in a brownish bottle. The cation exchange capacity (CEC) of this clay is 50.4 meq/100 g clay. HDTMA chloride (Aldrich Chemical Co., 25 wt%), a cationic surfactant, was used as an organic modifier. HDTMA-montmorillonite was prepared following the procedure of Kim et al. [1996]. The adsorption of HDTMA onto montmorillonite was performed in a 2-L batch reactor with 5,000 mg/L HDTMA solution. Thirty grams of washed montmorillonite was added to the reactor and then agitated with a mechanical stirrer at 500 rpm for 24 hours. After agitation, HDTMA-montmorillonite was collected and washed several times with 500 mL of distilled water and dried in an oven at 60 °C for 24 hours. The HDTMA-montmorillonite was kept in a brownish bottle before use. Organic carbon content (f_{oc}) of the HDTMA-montmorillonite was 11.41 (w/w%) based on the analysis by Huffman Laboratories, Inc. (Golden, CO, USA).

2. Sequential Sorption and Desorption in HDTMA-Montmorillonite

Single-solute sequential sorption and desorption experiments were conducted in 40-mL amber glass vials with Teflon-lined silicon septa (Fisher Scientific, Pittsburgh, PA, USA). To minimize the headspace, the vials containing 0.5 g of HDTMA-montmorillonite each were filled with stock solutions (4,000 mg/L for 2-CP and 400 mg/L for 2,4,5-TCP, respectively) and then shaken at 150 rpm on an orbital shaker for 24 hours at 20 °C. Preliminary kinetic experiments showed that sorption equilibrium was reached within 1 hour (data not shown). However, sorption was conducted for 24 hours throughout this study to ensure equilibrium. After reaching equilibrium, the vial was centrifuged at 2,000 rpm for 15 minutes and the aqueous phase equilibrium concentration was measured by UV absorbance (Hewlett-Packard, 8452A) at the isosbestic point of each solute. The solid phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase result from sorption onto the solid phase. After 90-95% of the supernatant was removed, the vial was refilled with the fresh stock solution to conduct the next sorption step. The sequential sorption process was repeated until desorption reversibility of sorbed CP was observed after several repetitive sorption steps (i.e., solution phase CP concentration at the last sorption step was greater than that at previous sorption steps). After the last sorption step, sequential desorption was conducted by using an electrolyte solution at two different pHs. Control experiments without HDTMA-montmorillonite were conducted to investigate loss of CPs due to sorption onto the surface of the glassware (data not shown). The concentration of CPs remained essentially unchanged. All experiments were run in duplicate.

Sequential desorption was conducted at 20 °C for 24 hours in an orbital shaker at 150 rpm. The sequential desorption steps were repeated until no significant amount of solute was observed in the solution. A bisolute stock solution (2-CP/2,4,5-TCP) with the same concentration of 400 mg/L each was prepared. Sequential sorption and desorption experiments for the bisolute systems were conducted following the same procedure for the single-solute system. The solid phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase result from sorption onto the solid phase. All experiments were run in duplicate.

3. Sorption and Desorption Models

Single-solute sorption and desorption equilibrium data were fitted to the Freundlich model:

$$q=K_F C^N \qquad (1)$$

where q (mg/g) is the equilibrium solid-phase concentration, C (mg/L) the equilibrium solution concentration, and K_F [$(mg/g)/(mg/L)^N$] and N (dimensionless) are Freundlich parameters.

Table 1. Physicochemical properties of chlorophenols used

Solute	MW	Solubility (mg/L)*	Density (g/cm^3)	log K_{ow}*	pK_a at 25 °C*	UV wavelength at isosbestic point (nm)
2-CP	128.6	11,300	1.241	2.15	8.56	278
2,4,5-TCP	197.4	1,200	1.50	3.72	7.00	296

*Data obtained from SRC PhysProp database (http://www.syrres.com).

The sorption and desorption model parameters were determined by using a commercial software package, Table Curve 2D® (Version 5.0, SPSS, Inc.).

4. Ideal Adsorbed Solution Theory

The IAST was used to predict the bisolute sorption and desorption equilibria using the single-solute isotherm data. The IAST originally proposed by Radke and Prausnitz [1972] is of descriptive nature and requires experimental equilibrium concentrations in the solution phase to predict solid phase concentrations. To utilize the full predictive power and to simplify the calculation, we followed a modification made by Yen and Singer [1984]. IAST based on the equivalence of spreading pressure in a mixture containing N solutes leads to:

$$\int_0^{q_1^*}\frac{d\log C_1}{d\log q_1}dq_1=\int_0^{q_2^*}\frac{d\log C_2}{d\log q_2}dq_2=A=\int_0^{q_N^*}\frac{d\log C_N}{d\log q_N}dq_N \qquad (2)$$

Other equations involved in IAST calculation are:

$$C_{m,i}=z_iC_i^*,\ \ \sum_{i=1}^{N}z_i=1,\ \ q_i^*=K_F(C_i^*),$$

$$\frac{1}{q_T}=\sum_{i=1}^{N}\frac{z_i}{q_i^*},\ \ q_{m,i}=z_iq_T=q_{m,i}^0+\frac{V(C_{m,i}^0-C_{m,i})}{W} \qquad (3)$$

In the above equations, $C_{m,i}$ and $q_{m,i}$ are equilibrium concentration in the liquid phase and in the sorbed phase of a solute i in a mixture, respectively. Superscript 0 in these variables represent initial concentration in N-solute sorption. In case of desorption, superscript 0 should be replaced by superscript d. z_i represents the mass fraction of solute i in the sorbed phase, and C_i^* and q_i^* refer to equilibrium concentrations in the liquid and solid phases of solute i that sorbs singly from solution at the same temperature and spreading pressure as those of the mixture, respectively. $C_{m,i}^0$ and $q_{m,i}^0$ are the initial concentrations of solute i in the solution and solid phases, respectively. The function f in $q_i^*=f(C_i^*)$ denotes a single-solute sorption model for solute i. q_T is the total sorbed concentration of all solutes in the mixture. V and W represent the solution volume and adsorbent weight, respectively. There are 5N+1 equations in total, while $C_{m,i}$, $q_{m,i}$, C_i^*, q_i^*, z_i, and q_T comprise a set of 5N+1 unknowns. Therefore, we can predict the multi-solute sorption and desorption equilibria, $C_{m,i}$ vs. $q_{m,i}$, by solving these equations simultaneously.

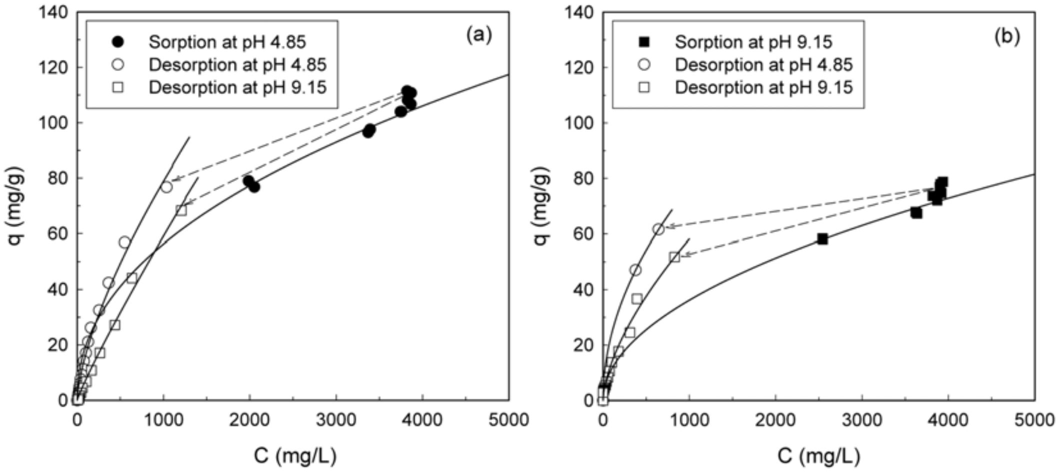

Fig. 1. Effect of pH on the sequential sorption and desorption of 2-CP in HDTMA-montmorillonite. (a) sorption at pH 4.85 and (b) sorption at pH 9.15, respectively. Lines indicate Freundlich model fitting.

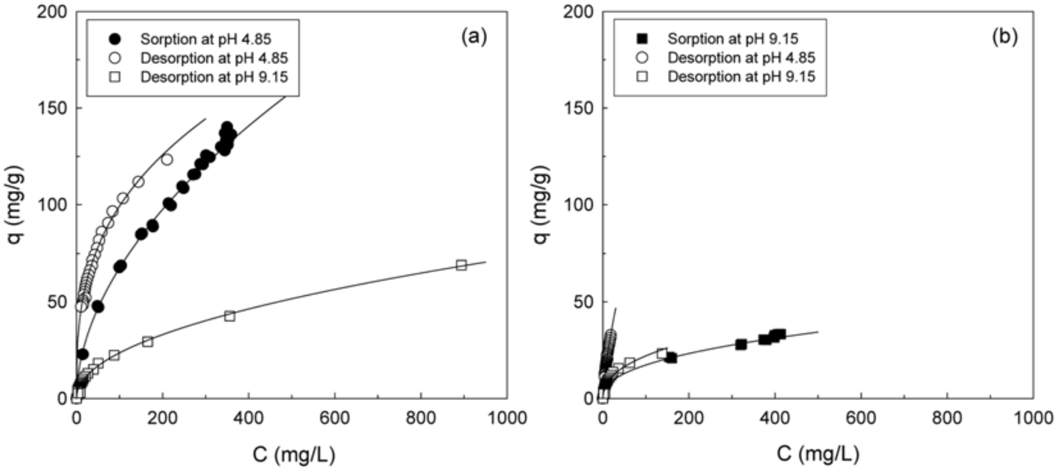

Fig. 2. Effect of pH on the sequential sorption and desorption of 2,4,5-TCP in HDTMA-montmorillonite. (a) sorption at pH 4.85 and (b) sorption at pH 9.15, respectively. Lines indicate Freundlich model fitting.

Table 2. Freundlich model parameters for multi-step sorption and desorption of chlorinated phenols in HDTMA-montmorillonite at two pH values

	Sorption					Desorption				
Solute	pH	K_F	N	R^2	SSE	pH	K_F	N	R^2	SSE
2,4-CP	4.85	1.546 (±0.513)	0.546 (±0.044)	0.993	69.91	4.85	0.736 (±0.108)	0.677 (±0.023)	0.987	101.3
						9.15	0.117 (±0.029)	0.901 (±0.036)	0.993	33.52
	9.15	0.441 (±0.307)	0.621 (±0.085)	0.987	64.73	4.85	2.366 (±0.000)	0.504 (±0.000)	1.000	0.000
						9.15	0.750 (±0.130)	0.630 (±0.028)	0.979	73.25
2,4,5-TCP	4.85	5.223 (±0.317)	0.553 (±0.011)	0.996	152.7	4.85	20.17 (±0.597)	0.346 (±0.007)	0.993	113.3
						9.15	2.391 (±0.110)	0.494 (±0.008)	0.995	25.31
	9.15	1.866 (±0.327)	0.475 (±0.030)	0.992	8.26	4.85	3.881 (±0.217)	0.732 (±0.023)	0.979	33.66
						9.15	3.115 (±0.168)	0.425 (±0.015)	0.959	32.38

Units: K_F=[(mg/g)/(mg/L)^N] and N (dimensionless). Number in parentheses=standard deviation.

RESULTS AND DISCUSSION

1. Single-Solute Sequential Sorption and Desorption

Figs. 1 and 2 show the single-solute sequential sorption and desorption data of 2-CP and 2,4,5-TCP at pH 4.85 (mostly neutral species) and 9.15 (predominantly anionic species: about 80% and 99% of 2-chlophenolate and 2,4,5-trichlorophenolate anions, respectively), respectively. Since we used the isosbestic point of each solute in determining solution concentration, the abscissa and ordinate of all the figures in this work should be understood as the total (i.e., neutral plus anionic forms) solution and solid-phase concentrations, respectively. Sorption affinity of 2,4,5-TCP was higher than that of 2-CP at both pHs. The higher sorption affinity of 2,4,5-TCP is attributed to stronger hydrophobic interaction as indicated by the K_{ow} values of the CPs (Table 1). Most neutral species are believed to dissolve in the pseudo-organic medium formed by the conglomeration of the long hydrocarbon chains of the HDTMA cation, while anionic species adsorb onto the two-dimensional surface of the pseudo-organic medium [Stapleton et al., 1994; Kim et al., 2001]. Since anionic species are more hydrophilic and soluble in water than neutral species, they may not readily dissolve or partition into the pseudo-organic phase, thereby causing less sorption affinity.

Sorption affinity of 2-CP and 2,4,5-TCP at pH 4.85 was higher than that at pH 9.15, respectively. The difference between the two solutes was attributed to the content of anionic species at pH 9.15 (i.e., 80% vs. 99%). Sorption isotherms at both pHs were nonlinear as indicated by *N* values of Freundlich model (0.48-0.77) in Table 2. As the pseudo-organic medium formed by long hydrocarbon tails of HDTMA cations had finite sorption capacity, desorption reversibility of CP was observed after several repetitive sorptions, i.e., the amount sorbed in the last sorption step desorbed reversibly (see Figs. 1 and 2).

After desorption reversibility was observed at the last sorption step, desorption experiments were conducted. To investigate the effect of pH on desorption, the pH in desorption stage was adjusted to the same as or different from the pH in the sorption stage. Single-solute sequential desorption data of the 2-CP and 2,4,5-TCP are shown in Figs. 1 and 2, respectively. As expected from the sorption experiments, the affinity of each solute in desorption stage was found to be in the order of pH 4.85>pH 9.15. Furthermore, 2,4,5-TCP was shown to have a higher affinity in desorption than 2-CP at both pHs. Even though saturated sorptions were obtained at either pH 4.85 or pH 9.15, both desorption isotherms were nearly identical within experimental error as long as the pH in the desorption

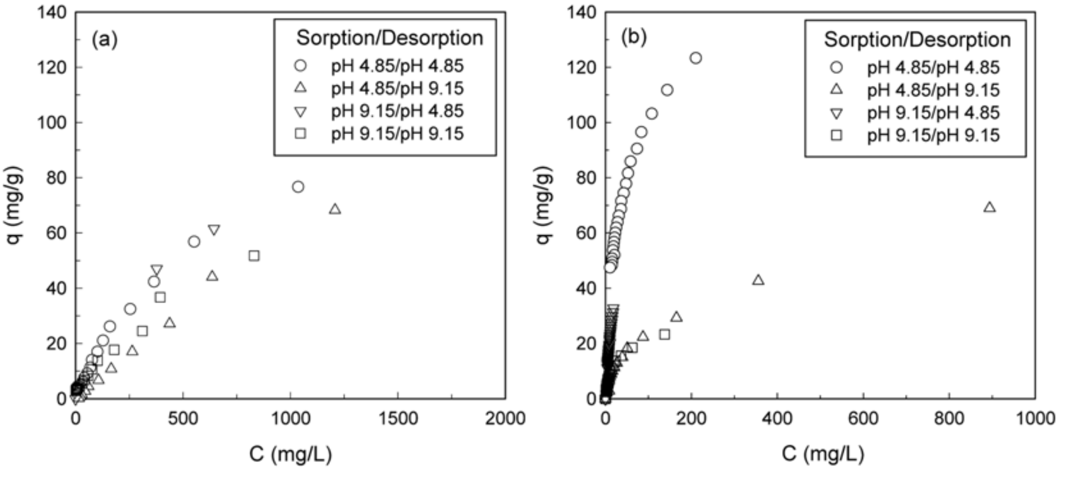

Fig. 3. Comparison of the sequential desorption of (a) 2-CP and (b) 2,4,5-TCP from HDTMA-montmorillonite at pH 4.85 and 9.15 after sorption at two pH values, respectively.

stage was the same (see Fig. 3 for comparison). This showed that desorption of both chlorophenols strongly depended on current pH in the desorption stage regardless of the pH history in the sorption stage. The solution chemistry of the IOC was in operation to satisfy a new equilibrium condition depending on the current pH. The solid-phase concentration was accordingly adjusted by shifting from the three-dimensional partition in the core (i.e., neutral species at pH 4.85) to the two-dimensional adsorption on the surface of the pseudo-organic medium (i.e., anionic species at pH 9.15) or vice versa.

Figs. 1 and 2 also show that there was no appreciable desorption-resistant fraction of chlorophenols in organoclays after sequential repetitive desorptions. We believe that HDTMA-montmorillonite organoclays do not show desorption-resistant fraction since the pseudo-organic phase formed by the conglomeration of the long hydrocarbon chains of the HDTMA cation is different from the “soft” or “hard” carbon in the usual soils and sediments in the desorption-resistance study. Desorption of CPs in HDTMA-montmorillonite was nearly reversible and no desorption-resistant fraction was observed. However, organoclays were found to exhibit the sorption-desorption hysteresis at the same pH (figure not shown). Freundlich model parameters for the single-solute sequential sorption and desorption of 2-CP and 2,4,5-TCP in HDTMA-montmorillonite are summarized in Table 2. A comparison of Figs. 1 and 2 shows that 2,4,5-TCP was more resistant for desorption than 2-CP at both pHs. A solute with higher K_{ow} exhibited a higher sorption affinity and a higher resistance for desorption in HDTMA-montmorillonite.

DiVibenzo and Sparks [2001] reported on the sorption and desorption of PCP (pK_a=4.75) on a natural soil at pH 4 and 8. Sorption of the neutral PCP species was linear due to partitioning into soil organic matter (SOM), while that of charged species was nonlinear and fitted with the Langmuir model due to adsorption. Desorption of the neutral form was completely reversible; however, the charged species exhibited desorption-resistant fraction. The difference in sorption and desorption between the neutral and charged species is attributed to the fact that the neutral form of PCP partitions by hydrophobic binding to the soil, while anionic form sorbs by a more specific exothermic adsorption reaction. You and Liu [1996] investigated desorptive behavior of chlorophenols in artificially contaminated soils. The amount of three chlorophenols (2,6-DCP, 2,4,6-TCP, and PCP) desorbed from soils increased with increasing pH from 3 to 11. Deprotonated chlorophenols were more labile or easily desorbing than their conjugated acids. The amount of chlorophenol adsorption decreased in the order of PCP>2,4,6-TCP>2,6-DCP. Hydrophobic interactions were found to be a major driving force of adsorption reactions, and thus hydrophobicity of chlorophenols is an important factor controlling their desorption-resistant fraction. Desorption increased with increasing pH from acidic to neutral conditions. The more hydrophobic the chlorophenol, the more significant the pH effect on its desorption. Desorption of DCP from geosorbent was hysteric and incomplete [Fytianos et al., 2000; Lagas, 1988; Danis and Albanis, 1997] with irreversible binding of solute attributed to enzymatic and abiotic reaction [Bhandari et al., 1996, 1997; Danis and Albanis, 1997; Palmo and Bhandari, 2000]. Bhandari et al. [1996] investigated the binding of 4-CP to organic matter during humification processes in soil. The incorporation of phenols into organic macromolecules occurs via covalent bond formation, and results from biologically or chemically catalyzed reactions. Nearly 15% of the soil-associated 4-CP was resistant to desorption. The unextracted 4-CP was incorporated into humic and fulvic acids and a second fraction associated with humin or soil mineral surface. Bhandari et al. [1997] quantified binding of phenol, 4-chlorophenol (4-CP), 2,4,6-trichlorophenol (TCP), and pentachlorophenol (PCP) to a sandy surface soil under aerobic and anoxic conditions, with and without autoclaving. The chemically bound contaminant was characterized as biologically or abiotically coupled. A portion of the residual contamination on soil was desorbable but mass transfer rate-limited. The amount of bound material that was resistant to desorption was at least twice as high in nonautoclaved soils under oxic conditions as compared to soil in systems from which O_2 or biochemical activity, or both had been eliminated. The amount of non-desorbing residue was dependent on the initial aqueous concentration of the contaminant.

Several conceptual models have been proposed in the literature to explain the desorption-resistance: (1) the existence of a condensed, glassy, organic polymeric matter as adsorbent. The adsorption to the condensed organic matter phase could be kinetically slow, site specific, and non-linear [Weber and Huang, 1996; Xing et al., 1996]; (2) the presence of high surface area carbonaceous material (HSACM, e.g., soot, charcoal and black carbon) in sorbent. The adsorption to these high surface area carbonaceous materials could be nonlinear, site specific, and limited in capacity [McGroddy et al., 1996; Chiou and Kile, 1998; Chiou et al., 2000; Allen-King et al., 2002; Kleineidam et al., 2002]; and (3) the sorbed chemicals are irreversibly trapped in the humic organic matrix following sorption (irreversible adsorption) [Kan et al., 1998]. The term “irreversible” is used to imply that desorption takes place from a molecular environment that is different from the adsorption environment, and that desorption is essentially completely prevented. The irreversible or desorption-resistant compartment has been found to contain a finite maximum capacity [Kan et al., 1997]. Neutral hydrophobic organic compounds desorb at a similar limit, regardless of the physical/chemical properties of the chemicals. Desorption-resistant fraction was observed in natural soils and sediments [Bhandari et al., 1996, 1997; Danis and Albanis, 1997; Kan et al., 1997; 1998; DiVincenzo and Sparks, 2001; Fytianos et al., 2000; Palmo and Bhandari, 2000]. In this study, however, both neutral and anionic speciation of chlorophenols in HDTMA-montmorillonite was completely desorbing. The pseudo-organic medium formed by the conglomeration of the long hydrocarbon chains of the HDTMA cation represents an amorphous “rubbery” organic polymer matter without a condensed glassy phase or HSACM. Moreover, since sorbed phenols are not irreversibly trapped in the pseudo-organic medium, desorption-resistant fraction was not observed in HDTMA-montmorillonite.

2. Bisolute Sequential Sorption and Desorption

Bisolute sequential sorption experiments were conducted until a less strongly sorbed solute (2-CP) desorbed from HDTMA-montmorillonite due to competition. At the end of sorption stage, a solute with the weaker sorption affinity first desorbs as the other solute with the stronger sorption affinity still sorbs displacing the weaker one. A bisolute sequential sorption and desorption behavior at pH 4.85 (mostly neutral or protonated species dominant) was selected and shown together in Fig. 4. Affinity in sorption and desorption of a solute in the bisolute system was reduced compared to that in the

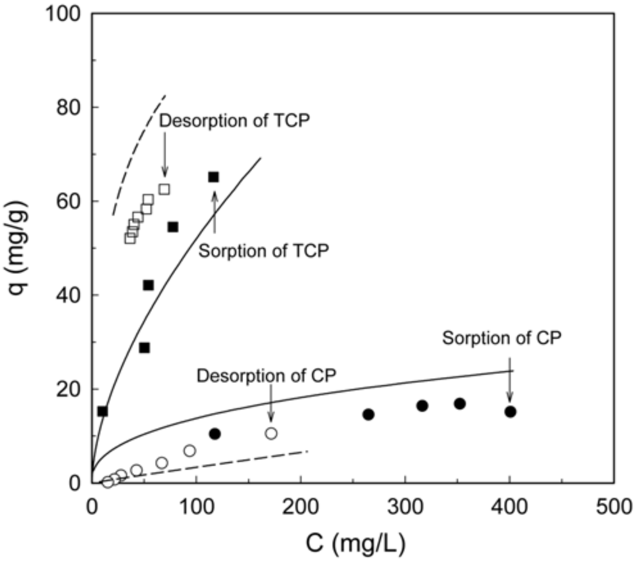

Fig. 4. Sequential bisolute sorption and desorption of 2-CP/2,4,5-TCP in HDTMA-montmorillonite at pH 4.85. Solid and dashed lines represent bisolute Freundlich-IAST model predictions for sorption and desorption, respectively.

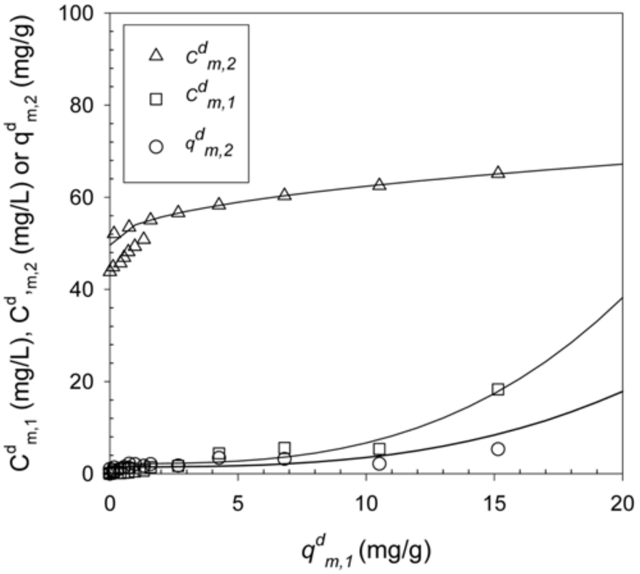

Fig. 5. Functional relations between experimental data for sequential bisolute desorption from HDTMA-montmorillonite. ($C^d_{m,2}$ and $C^d_{m,2}$=initial concentrations of 2-CP and 2,4,5-TCP, respectively. $q^d_{m,1}$ and $q^d_{m,2}$ are initial sorbed concentrations of 2-CP and 2,4,5-TCP, respectively).

single-solute system due to the competition between solutes (Figure not shown separately). Furthermore, the solute (2-CP) with a lower sorption affinity in the single-solute system exhibited a greater reduction in both sorption and desorption amount.

The IAST coupled with the single-solute Freundlich model (Freundlich-IAST model) was employed to predict the bisolute sorption and desorption equilibria. The single-solute Freundlich model parameters were previously determined from the nonlinear curve fitting to the single-solute sequential sorption data (see Table 2).

In order to implement the IAST predictions, the following functional relationships should be provided: $C^0_{m,2}=f(C^0_{m,1})=g(q^0_{m,1})$ and $q^0_{m,2}=h(q^0_{m,1})$, where superscript 0 denotes initial concentration in the case of sorption. For the bisolute sorption protocol we have chosen (i.e., the fixed weight of sorbent and the varying initial concentrations satisfying $C^0_{m,1}=C^0_{m,2}$), the functional relationships become $C^0_{m,1}=C^0_{m,2}$ and $q^0_{m,1}=q^0_{m,2}=0$ for the fresh sorbents. To compare predictions with the experimental data, we computed the sum of squared errors (SSE) from the following equations [Kleibaum and Kupper, 1978] and listed them in Table 3.

$$\mathrm{SSE}=\sum(q_i-\tilde{q}_i)^2 \tag{4}$$

In the above equation, $\tilde{q}_i$ denotes the IAST-predicted uptake of a solute.

Bisolute sequential desorption data were compared with the IAST predictions. Single-solute isotherms coupled to the bisolute predictive IAST were the Freundlich model, the parameters of which were previously determined by curve fitting to the single-solute sequential desorption data (listed in Table 2). Fig. 5 shows the functional relations for the prediction of bisolute sequential desorption, following functional relationships should be provided: $C^d_{m,2}=f(C^d_{m,1})=g(q^d_{m,1})$ and $q^d_{m,2}=h(q^d_{m,1})$. The superscript d denotes initial concentrations for desorption experiment. As mentioned previously, these experimental relations are necessary for the IAST predictions in the bisolute sequential desorption.

Table 3. SSE values for competitive sequential sorption and desorption of 2-CP/2,4,5-TCP predicted by Freundlich-IAST model (pH=4.85)

Solute	Compounds	Sorption	Desorption
2-CP/2,4,5-TCP	2-CP	79.99	75.66
	2,4,5-TCP	236.2	1,987

To compare the performance of the IAST predictions with the bisolute sequential sorption/desorption data, the SSE values were computed (Table 3). The Freundlich-IAST predictions for the bisolute sequential sorption and desorption at pH 4.85 were positively correlated with the experimental data.

CONCLUSIONS

The sequential single- and bisolute sorption/desorption of 2-CP/2,4,5-TCP under controlled pH conditions (4.85 and 9.15) was conducted by using montmorillonite modified with HDTMA cations. By the modification, the surface property of montmorillonite was changed from hydrophilic to organophilic, thus enhancing the sorption capacity for the organic contaminants. Affinity of 2,4,5-TCP in sorption and desorption at both pH conditions was found to be higher than that of 2-CP as inidcated by the octanol to water partition coefficient (K_{ow}). For the two chlorinated phenols chosen in this work, neutral species at pH 4.85 exhibited higher affinity to HDTMA-montmorillonite in both sorption and desorption than anionic species predominant at pH 9.15 (i.e., about 80% and 99% anionic forms of 2-CP and 2,4,5-TCP, respectively). Desorption of both chlorinated phenols was found to be strongly dependent on the present pH in the desorption stage, regardless of the pH history in the sorption stage. No appreciable desorption-resistant fraction of chlorophenols in HDTMA-montmorillonite was observed after sequential repetitive desorption because the inherent nature of the pseudo-organic medium in the organoclays is different from soil organic matter. Affinity in both sorption and desorption of a solute in the bisolute system was reduced compared to that in the single-solute system due to the competition between solutes. The solute with a lower sorption affinity exhibited a greater reduction in both sorption and desorption amount. IAST coupled with single-solute Freundlich model was positively correlated with the multi-step sorption and desorption equilibria in the bisolute system.

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